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Testing links between the pre-GOE iron cycle and oxygenation using triple iron isotopes

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The role that iron played in Earth's oxygenation is complex, because while consuming O_2 during oxidation reactions, it may also have indirectly promoted atmospheric oxygenation via pyrite burial. Iron isotopes may illuminate these competing aspects of the Archean iron cycle, as sediments predating the Great Oxygenation Event (GOE) have a huge range of $\delta^{56}Fe$ values, including extreme isotopically depleted pyrites [1]. Those depletions were variably interpreted as tracers of progressive Fe^{3+}-oxyhydroxide removal [1]; dissimilatory iron reduction [2]; or kinetic isotope effects during sulfide-limited pyrite precipitation [3]. Distinguishing these processes is not possible using a single isotope ratio. We developed high-precision triple iron isotope measurements which can distinguish between fractionations that were driven by equilibrium effects including Fe^{2+}-Fe^{3+} redox reactions, and kinetic isotope effects that drive fractionations during pyrite precipitation, because these processes follow different mass fractionation laws [4]. Depleted pre-GOE pyrites fall in an intermediate triple iron isotope space between the two endmember mass fractionation arrays determined for Fe^{3+}-oxyhydroxide removal and kinetic pyritization. This suggests that pre-GOE pyrites record important influences of both marine iron oxidation and sulfide limitation. Using an fractionation model informed by these data, we estimated the relative sizes of sedimentary Fe^{3+}-oxyhydroxide and pyrite sinks for Neoarchean marine iron. Triple Fe isotope measurements of individual pyrites provide snapshots of the iron sulfide sink through time, and they are consistent with other datasets indicating increasing sulfide availability in pyrite-forming environments in the runup to the GOE [5]. By considering the redox balance of the calculated iron sink sizes, we suggest that pyrite burial could have promoted O_2 export exceeding local Fe^{2+} oxidation sinks, and thus may have contributed to early episodes of transient oxygenation of Archean surface environments [6].

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